COMPUTER SIMULATION OF MULTIMERS
SPUTTERED FROM COPPER

Calvin Bricker Delaplain

NAVAL POSTGRADUATE SCHOOL
Monterey, California

THESIS

COMPUTER SIMULATION OF
MULTIMERS SPUTTERED FROM COPPER

by

Calvin Bricker Delaplain

June 1975

Thesis Advisor: D.E. Harrison, Jr.

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Computer Simulation of Multimers Sputtered From Copper		5. TYPE OF REPORT & PERIOD COVERED Master's Thesis; June 1975
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Calvin Bricker Delaplain		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Postgraduate School Monterey, California 93940		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Postgraduate School Monterey, California 93940		12. REPORT DATE June 1975
		13. NUMBER OF PAGES 59
14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Sputtered Multimer Mechanisms
Sputtering Simulation
Sputtered Multimers

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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(Page 1) S/N 0102-014-6601 |

(20. ABSTRACT Continued)

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     Nearest neighbor atoms in the crystal rarely formed dimers
or trimers. Next nearest neighbor clustering was much more
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     Members of a multimer usually were not emitted simultaneously.
Often four or five collisions by the ion or its primary knock-on
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relatively slow speed of the emitted atoms still allowed cluster
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Computer Simulation of
Multimers Sputtered From Copper

by

Calvin Bricker Delaplain
Captain, United States Army
B.S., United States Military Academy, 1967

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN PHYSICS

from the

NAVAL POSTGRADUATE SCHOOL
June 1975

ABSTRACT

The formation of clusters of sputtered atoms, called multimers, has been investigated in a digital computer simulation of single crystal copper bombarded with argon ions. Five formation mechanisms for sputtered dimers and four formation mechanisms for sputtered trimers were identified and analyzed in detail. The mechanisms did not reveal a single case in which a multimer was formed by the motions of a single ion or atom. Multimers were found to be caused by various interactions of the projectile ion with atoms in the first four layers of the crystal.

Nearest neighbor atoms in the crystal rarely formed dimers or trimers. Next nearest neighbor clustering was much more common.

Members of a multimer usually were not emitted simultaneously. Often four or five collisions by the ion or its primary knock-on atoms would intervene between the emission events, but the relatively slow speed of the emitted atoms still allowed cluster formation.

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ACKNOWLEDGEMENTS

I am indebted to the personnel of the Computer Facility, Naval Postgraduate School for the numerous computer runs.

I am especially grateful to Dr. Don E. Harrison, Jr., Professor at the Naval Postgraduate School for his supervision and assistance in this project. The many hours we spent together discussing the work along with his patience and tolerance were a great inspiration.

My appreciation also to my wife, Sudarat Delaplain, for her perserverance throughout the period of this research effort.

I. INTRODUCTION

Material is lost from a target which undergoes ionic
bombardment. This process is called sputtering. Rates of
sputtering have been determined for a variety of target
materials, using various incident ions with different
initial kinetic energies and angles of incidence. The
results of such measurements are generally reducible to
a "sputtering ratio," which may be defined as the number
of target atoms sputtered per incident ion.

A typical early experiment of this type was reported
by Yonts, Normand, and Harrison [11], who determined
sputtering ratios for copper undergoing ionic bombardment
with ion energies in the range of 5-30 keV. The data
included bombardment of copper by He^+, N^+, Ar^+ as well as
other ions. They concluded that initially at low energies,
the sputtering ratio increases quite rapidly with an
increase in ion energy. In the intermediate range (15-30
keV) the sputtering ratio remains fairly constant as
increased production is offset by increased penetration of
the ion. At still higher energies, the cross section ratio
for beam and lattice ion decreases, penetration dominates
production and the sputtering ratio falls off.

The mass spectra of the sputtered material from a target
crystal undergoing ionic bombardment frequently shows not
only the atomic species of the target material but also

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molecules of the material. These molecular species which may be comprised of many atoms are called "clusters" or "multimers."

In 1964, Woodyard and Cooper [10] studied low energy (0-100 eV) sputtering of polycrystalline copper. They showed that the ejected copper atoms were sputtered directly by the Ar^+ from the target as neutral copper atoms and that the threshold ion energy for sputtering was 27 eV. At ion energies greater than 50 eV they detected the presence of sputtered diatomic copper molecules.

Later, in 1968, Hortig and Muller [6] bombarded a cesium coated silver target with energetic krypton ions and were able to observe clusters, with as many as sixty atoms, of negatively charged silver ions in a mass spectrometer. The most striking feature reported was the difference in the fraction of clusters with odd and even numbers of atoms. The odd clusters dominated throughout the measured range.

Paralleling the experimental investigation of the sputtering ratio and the development of mass spectrographic analysis, was the use of computer simulation to model collisions between atoms in a crystal lattice.

In 1960, Gibson, Goland, Milgram and Vineyard [1] built a computer model to represent metallic copper and studied radiation damage events at low and moderate energies, up to 400 eV. The radiation damage event started with all of the atoms on their lattice sites with all but one of them at

rest. That one atom was initially endowed with an arbitrary kinetic energy and direction of motion, as though it had been struck by a bombarding particle.

In 1967, Harrison, Levy, Johnson, and Effron [4] used a digital computer to simulate the collisions between a bombarding argon ion and the target copper atoms. Through the computer simulation, actual mechanisms which caused sputtering were isolated and identified. Surface-layer atom and atoms near to the surface were found to be the only atoms participating in the sputtering event. For ion energies less than 40 keV, the sputtering processes predominantly took place within three atomic layers of the surface.

This work was extended in 1972 by Harrison, Moore, and Holcombe (HMH) [5] to a more precise model which included the attractive portion of the Cu-Cu potential function. The agreement between the simulation results and experimental data improved but the original interpretation of the low energy sputtering remained essentially unchanged.

The existence of multiatomic clusters in sputtered material has been well established. However, the mechanism by which clusters are formed, even the basic dimers, have not previously been identified.

Staudenmaier [9] proposed a kinetic model based on collision cascades to account for cluster formation. When a collision cascade arrived at the target surface there existed a high probability that two or more atoms received

approximately the same momentum (in magnitude and direction) at the same time. These atoms then left the surface as an aggregate which needed less expenditure of energy than for the emission of the separate atoms.

Können, Grosser, Haring, DeVries and Kistemaker [8] expanded on the kinetic model and suggested that dimers would likely be formed by sputtering of neighboring particles because they would have the strongest interaction.

Kaminsky [7] predicted that the copper dimer production was partially due to "gas-blister" explosions. Indications were that the bombarding atoms coalesce in the lattice and form migrating gas bubbles which explode upon reaching the target surface. Such explosions might also eject small clusters from the target material at thermal energies. While the "gas blister" theory is quite applicable to high intensity ion beams, this computer simulation effort was concerned with individual particle kinematics.

Until recently the sputtering ratio and the importance of the focuson mechanisms have been a major object of simulation sputtering studies. The present investigation was undertaken to identify mechanisms which cause the formation of sputtered multimers. A digital computer was used to simulate collisions between a bombarding argon ion and the target atoms in a copper microcrystallite. Primary effort was directed towards:

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1) Identification of mechanisms by which two stationary particles would move off together in a bound state after bombardment by a single atom.

2) Correlation of the mechanisms found above with the results of sputtering simulation in a small microcrystallite to determine whether the same mechanisms could actually produce multimers from a crystal surface under ion bombardment.

II.   NATURE OF THE SIMULATION

A target microcrystallite lattice is established whose sites represent the equilibrium positions of copper atoms near the surface of a face-centered-cubic, (100) orientation crystal. Atomic spacing is that determined by x-ray crystallographic studies (for copper, $\underline{a}$ = 3.615 A°). The target is represented by a composite potential function consisting of the Born-Mayer type Gibson-Number-two repulsive potential, a cubic matching potential with the four coefficients chosen to match potential and force (slope) at the junctions, and a Morse attractive potential as calculated by Girifalco and Weizer [2]. The method and resultant function have been discussed in detail in HMH [5].

Each ion of the beam is represented by a single neutral argon atom whose velocity vector determines the point of impact. The Ar-Cu interaction was determined by the Kinetic Secondary Electron (KSE-B) Potential [3]. (To avoid confusion with target atoms, the term $\underline{ion}$ is used interchangeably with $\underline{bullet}$ for the incident particle throughout this thesis.)

Successive runs are made using different ion energies, velocity vectors and impact points to simulate a wide range of collision possibilities. See references #1 and #5 for further details of the simulation model. The actual program is equivalent to the REAL model discussed in detail in Ref. 5.

After the computer run of the sputtering simulation was completed, a test was made to determine whether a multimer had been formed. Sputtered target atoms have random motion but there is a possibility that they will be close together and moving with nearly the same velocity. If the relative kinetic energy of these particles is less than the attractive potential energy binding them, they will stick together and form a vibrationally and rotationally excited dimer. A test which compares the relative kinetic energy and the binding energy of the sputtered atoms was made on all of the possible pair of combinations. In addition to dimer formation, if two different atoms each formed a dimer with a common third atom, the three atoms were assumed to exist as a trimer.

Reports of sputtering studies often include ad hoc formulations of mechanisms which are used to explain the formation of sputtered multimers. The sputtering process is discussed in this thesis in terms of mechanisms which have been observed to sputter dimers and trimers in the simulation. The ability to observe these mechanisms is an advantage peculiar to the computer simulation because each crystal atom is identified by a number for the mathematical calculation, and its complete track can be labeled and recorded. The tracks of selected atoms can be plotted to show the dynamics of the mechanism which caused the atoms to leave the surface as a cluster. The interactions which were observed to cause a sputtered dimer and/or trimer are the prime observable quantity of the simulation.

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The following detailed descriptions of formation mechan-
isms for sputtered trimers and dimers clearly shows this
advantage of the computer simulation.

III.   FORMATION MECHANISMS

A preliminary simulation was run with a 4x4x4 copper crystal made up of thirty-two atoms in a fcc(100) orientation. The bullet argon ion had an initial kinetic energy of 300 eV with a trajectory normal to the surface plane of the crystal. The bullet ion was initially positioned at a point above the surface and given the proper velocity vector to strike the corner atom #2 (located at 0,0,0) of the crystal and to drive that atom down and inward toward the center of the microcrystallite.

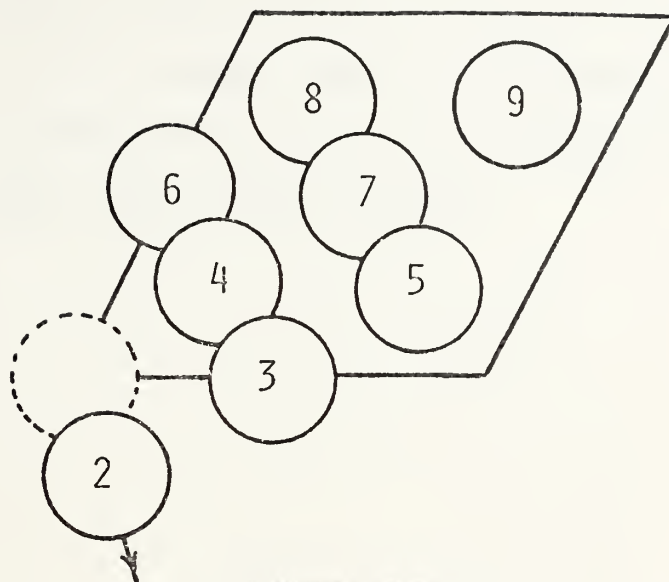The following drawings with explanations describe a trimer formation in detail.
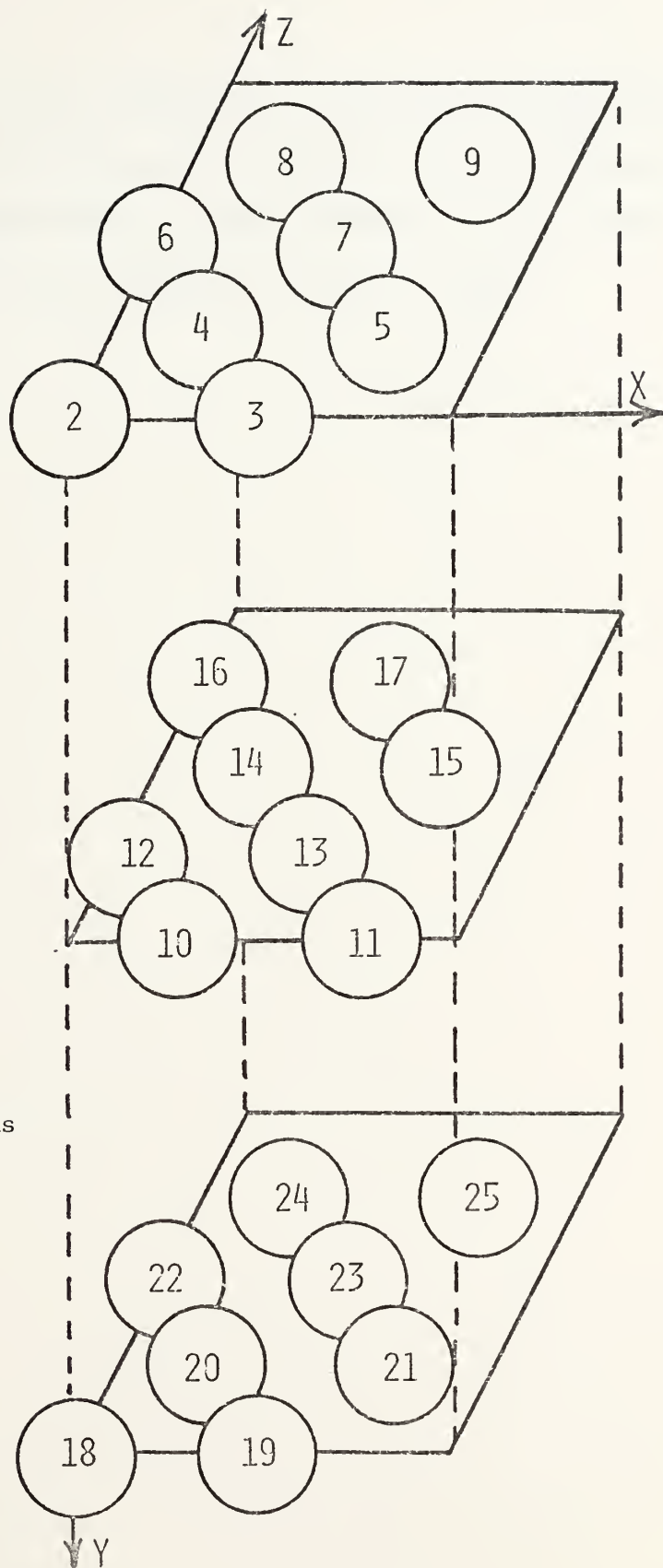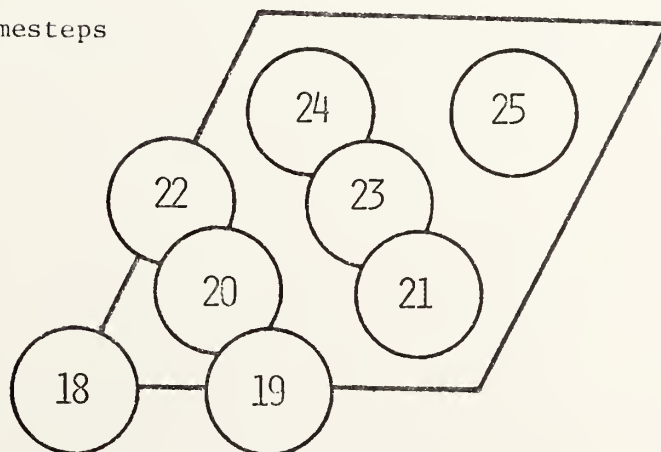
Initial Positions of Atoms

Fig. 1

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The argon ion has completed a glancing collision with
atom #2 and is now moving away from the crystal itself.
Atom #2 was driven down into the crystal at an almost
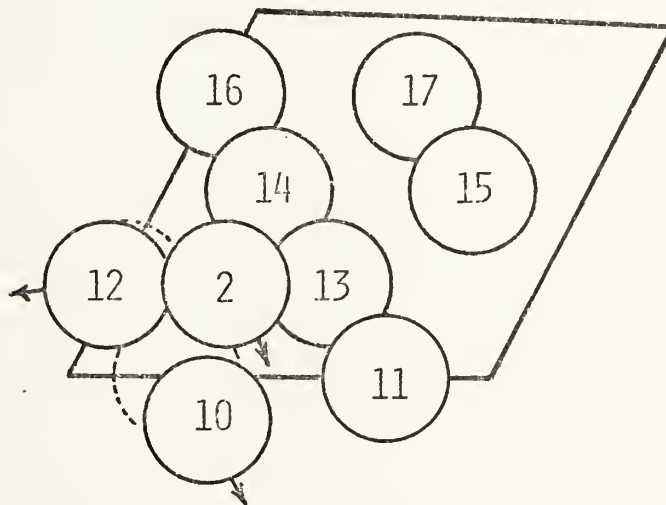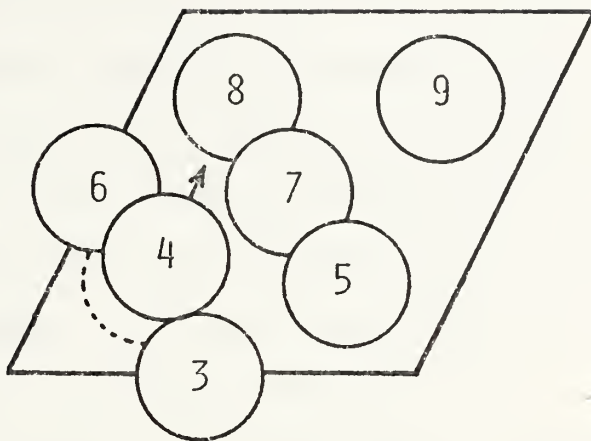perfect 45° angle with respect to the xz plane.
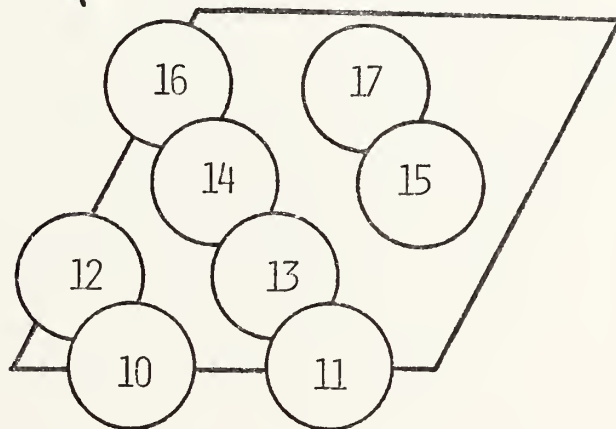
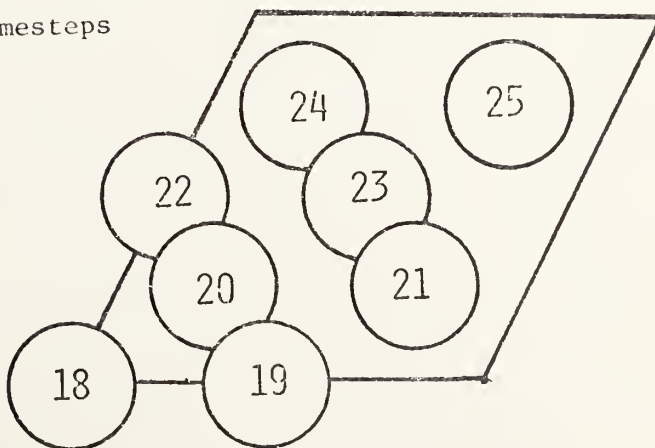Position of Atoms: 20 Timesteps

Fig. 2

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Atom #2 has passed under atom #4 pushing atom #4 upward, which is away from the crystal. Atom #2 has moved to the second layer and is pushing both atoms #10 and #12 downward away from the surface and into the crystal.
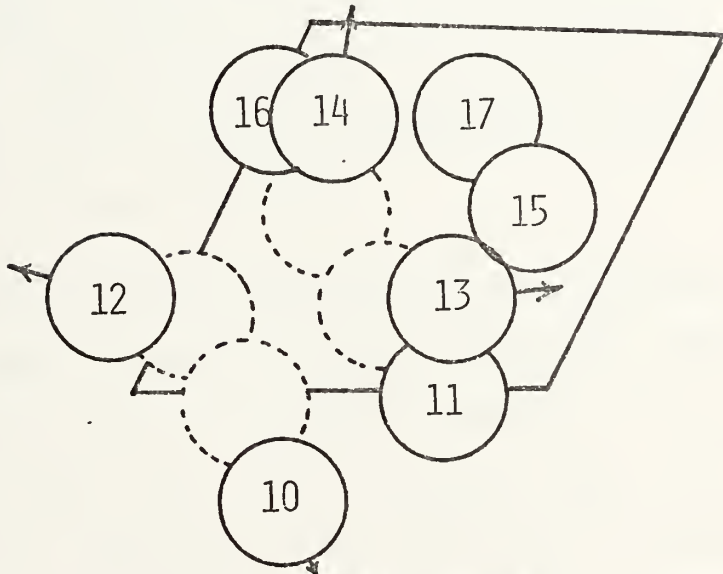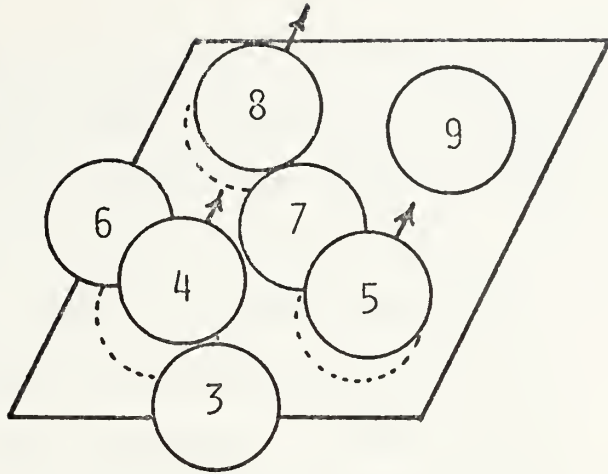
Position of Atoms: 30 Timesteps

Fig. 3

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Atom #2 is now beneath the third layer of atoms. After colliding with atoms #10 and #12 it burrowed under atoms #13 and #14 pushing them upward toward the surface. These atoms moving upward in turn push up on atoms #5 and #8. Symmetry causes atoms #5 and #8 to sputter in a common direction, which happens to be very closely parallel to the direction of the first sputtered atom #4.

Studies in the center of a larger microcrystallite indicate that the recoiling atoms #10 and #12 do not influence this trimer formation mechanism.

Position of Atoms: 45 Timesteps

Fig. 4

23
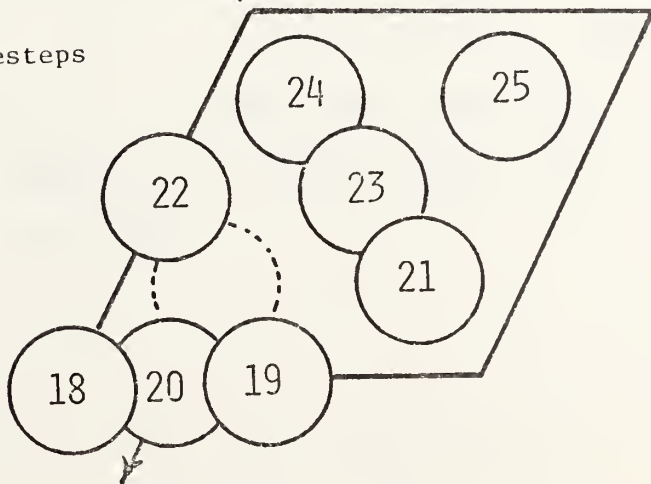
Final Status

Atoms #4, #5, and #8 have been sputtered away from the surface. Each possible pair combination was examined in its local center of mass coordinate system to determine whether the two atoms in the pair were bound. In both cases (4-5) and (4-8), the relative kinetic energy was less than the attractive potential energies binding the atoms so each pair of atoms was bound together. In this case, since atom #4 is common to both the atom #5 and atom #8 pairs, a trimer has been formed.

This trimer may not be stable over a long time period because it consists of a pair of coupled oscillators, but it leaves the surface as a unit.

The general lattice is shown in Fig. 5 with each atom numbered to show its initial lattice position. The bullet ion is not shown but it is given the number (1) in all computer simulation runs. The following pages show various dimer and trimer formation mechanisms that were observed in computer simulation runs of a bullet argon ion impacting normal to the surface of a representative copper micro-crystallite. An impact point which produces the multimer is indicated on each figure.
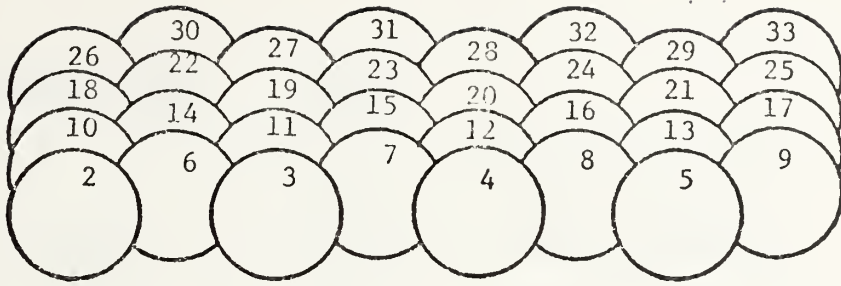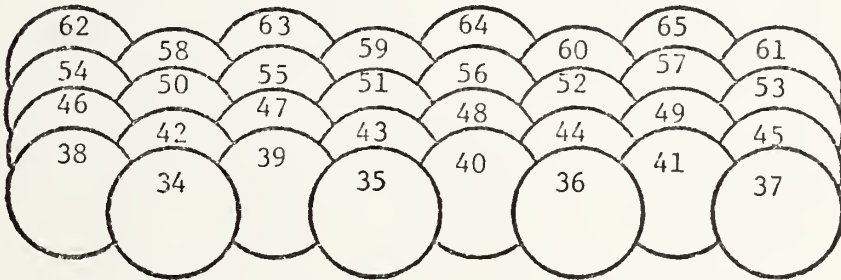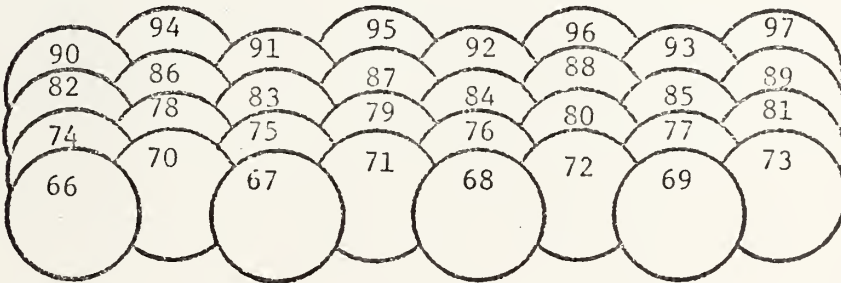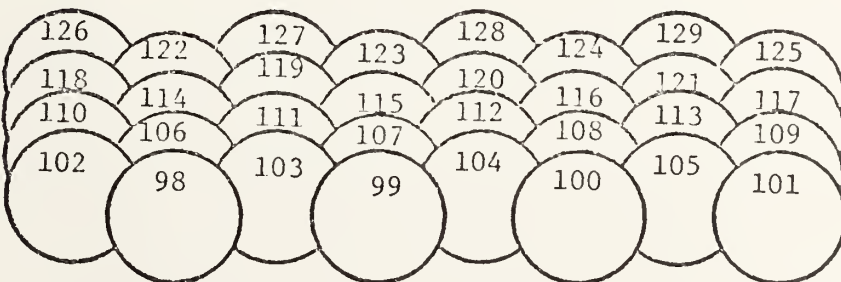
Numbering of Atoms in Microcrystallite

Fig. 5

DIMER MECHANISMS

Nomenclature	Atoms		
D #1	15-29	Fig. 6, page 27
D #2	12-20	Fig. 7, page 29
D #3	12-13	Fig. 8, page 33
D #4	22-30	Fig. 9, page 35
D #5	20-21	Fig. 10, page 38
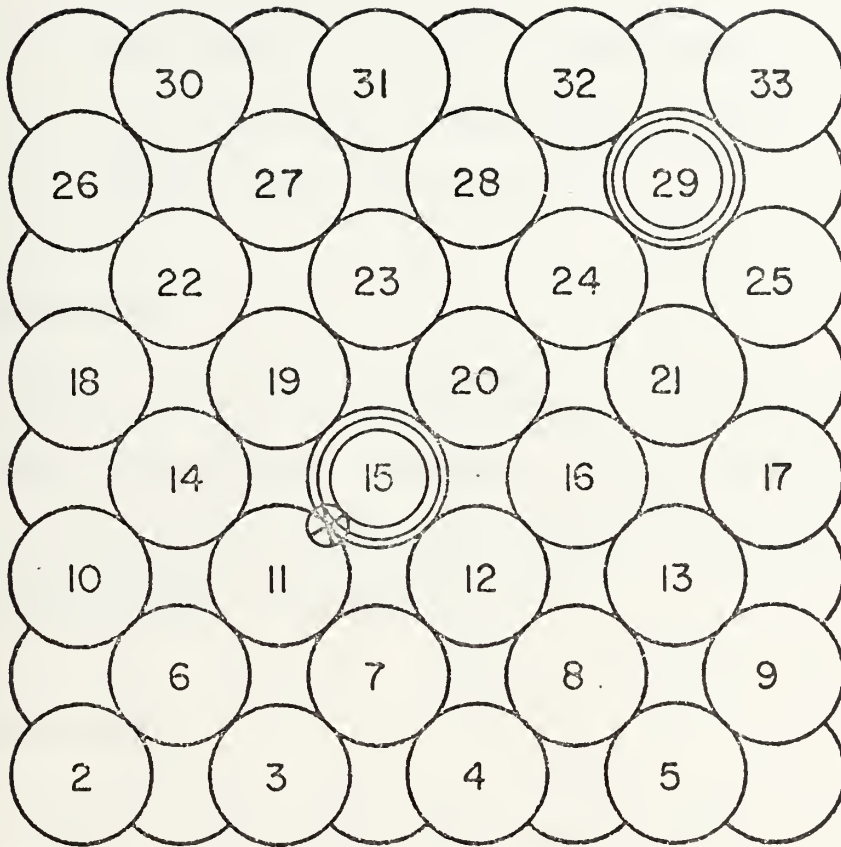
D #1

Initial Location of Dimer Atoms and Impact Point

Fig. 6

Initial Setup

8x4x8 copper crystal

129 atoms in fcc(100) orientation

Initial Energy of Argon Ion = 750 eV

Impact Point (2.5,0.0,2.5)

Timestep #30

The argon ion has penetrated the first and second layers of the target atoms. Atoms #11 and #15 have been driven down into the crystal. Atom #20 was lifted up when atom #15 was driven down and under it.

Timestep #60

Atom #15 has slowed down passing between atoms #52 and #56 and is now recoiling upward from atoms #84 and #88. Atom #24, after being pushed downward by the upward motion of atom #20 is now passing under and lifting atom #29.

Timestep #100

Atom #15 has now recoiled enough to push through the surface layer and is close enough in position and velocity to form a dimer with atom #29 which has also lifted away from the surface.

D #2

Initial Location of Dimer Atoms and Impact Point

Fig. 7

Initial Setup

8x4x8 copper crystal

129 atoms in fcc(100) orientation

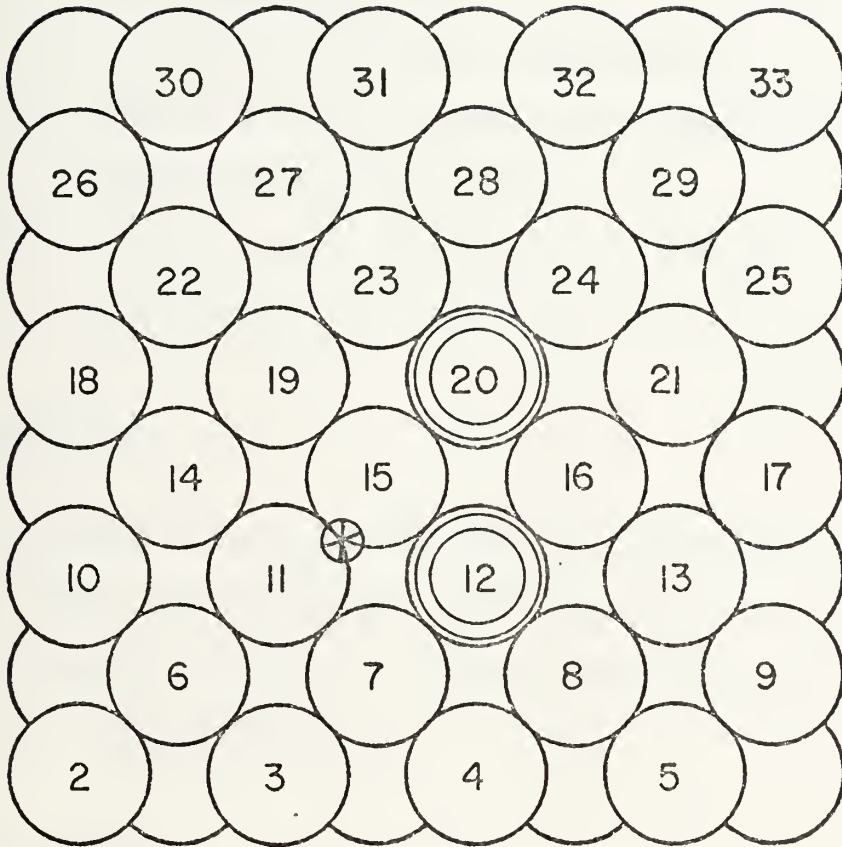(a) Initial Energy of Argon Ion = 400-515 eV

Impact Point (2.6,0.0,2.3)

(b) Initial Energy of Argon Ion = 500 eV

Impact Point (2.585-2.675,0.0,2.3)

Timestep #20

The bullet argon pushes down on atoms #11 and #15 and then passes under atom #12 lifting it up. Atom #11 is pushing down on atom #42 and atom #20 is beginning to feel atom #15 moving under it.

Timestep #40

The bullet ion has passed under the second layer pushing atom #12 away from the surface. Atom #15 has passssed under atom #20 pushing it off of the surface in such a manner that it forms a dimer with atom #12.

Note: Detailed data were taken on this rather simple dimer mechanism as shown in the "initial setup." This mechanism could be found over an energy range of ion energy from 400 eV

to 515 eV. With an ion energy of 500 eV the x-coordinate
of the impact point could vary from 2.585 to 2.675 lattice
units.

D #2 (12-30)   Detailed Data

Ion Energy (eV)	Impact Point	Potential Energy Excess (Dimer)
390	(2.6,0.0,2.3)	→ + 0.013
400	(2.6,0.0,2.3)	− 0.003
450	(2.6,0.0,2.3)	− 0.198
480	(2.6,0.0,2.3)	− 0.268
490	(2.6,0.0,2.3)	− 0.273
500	(2.6,0.0,2.3)	− 0.236
505	(2.6,0.0,2.3)	− 0.202
510	(2.6,0.0,2.3)	− 0.148
515	(2.6,0.0,2.3)	− 0.112
520	(2.6,0.0,2.3)	→ + 0.020
	(2.575,0.0,2.3)	→ + 0.128
500 eV	(2.585,0.0,2.3)	− 0.045
	(2.590,0.0,2.3)	− 0.129
	(2.595,0.0,2.3)	− 0.173
	(2.600,0.0,2.3)	− 0.236
	(2.625,0.0,2.3)	− 0.287
	(2.650,0.0,2.3)	− 0.173
	(2.675,0.0,2.3)	− 0.042
	(2.680,0.0,2.3)	→ + 0.010
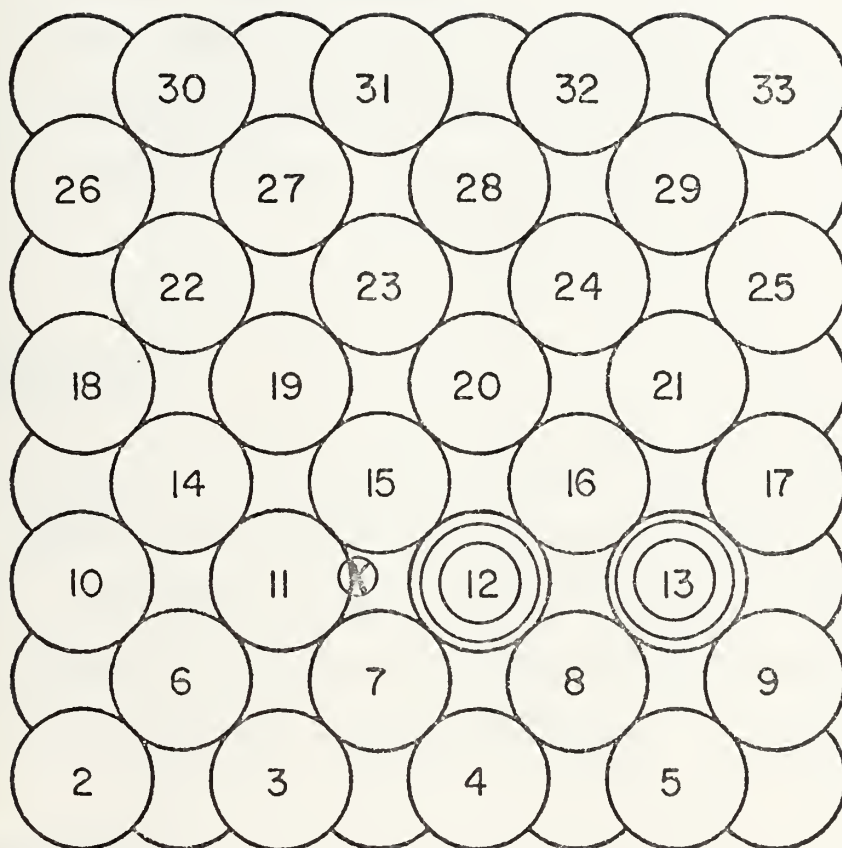
D #3

Initial Location of Dimer Atoms and Impact Point

Fig. 8

Initial Setup

> 8x4x8 copper crystal
>
> 129 atoms in fcc(100) orientation
>
> Initial Energy of Argon Ion = 750
>
> Impact Points   (2.8,0.0,2.0)
>
>   (2.9,0.0,2.0)

Timestep #20

The bullet ion initially drives atoms #7, #11 and #15 all downward and recoils off of atom #43 in the second layer. Atom #43 is driven strongly downward and the bullet ion on recoil hits atoms #7, #12, and #15 giving them an upward velocity away from the surface.

Timestep #70

Atom #43 has passed by atoms #107 and #108, pushing down on #107 and lifting up on #108. On coming up atom #108 pushes up atom #77.

Timestep #80

Atom #77 pushes up on atoms #41, #45 and #49 passing between them and then pushes up on #13 in such a manner that #13 binds with atom #12 which was pushed up earlier; so they can form a dimer.

D #4

Initial Location of Dimer Atoms and Impact Point

Fig. 9

Initial Setup

8x4x8 copper crystal

129 atoms in fcc(100) orientation

Initial Energy of Argon Ion = 5000 eV
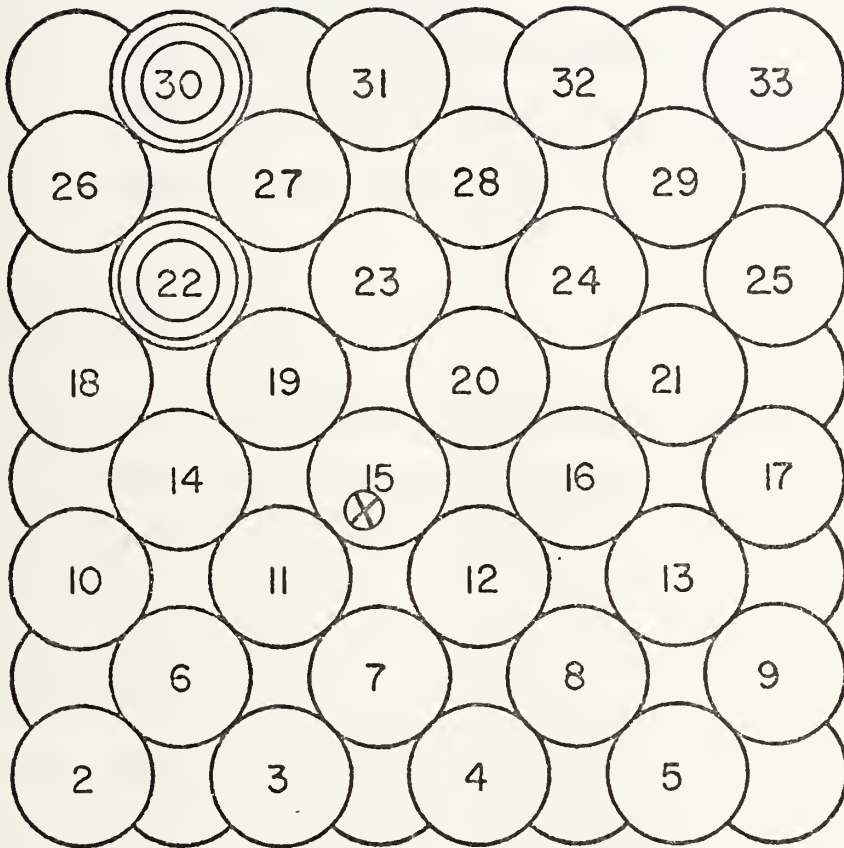
Impact Point (2.9,0.0,2.7)

Timestep #20

The bullet ion has penetrated the surface layer driving atom #15 down and lifting up atom #11. The bullet continues to the second layer pushing down on atom #43.

Timestep #70

Atom #15 has been pushed down to the third layer and drives atom #83 down into the crystal. The bullet ion has also moved down past the third layer and it has driven atom #75 downward. However atom #75 recoils off energetic third layer atoms and moves up toward the surface pushing up atom #50 on the way upward.

Timestep #150

Atom #50 lifts atom #22 up and away from the surface. Atom #30 is also lifted up and away from the surface by the action of third layer atoms and binds with atom #22 to form a dimer.

Mechanisms which involve second, third, and fourth layer atoms can be extremely complicated and interactions and collisions of the binary type are extremely rare. It is often possible for an atom to recoil in several directions within the crystal during the time interval of only a few timesteps.
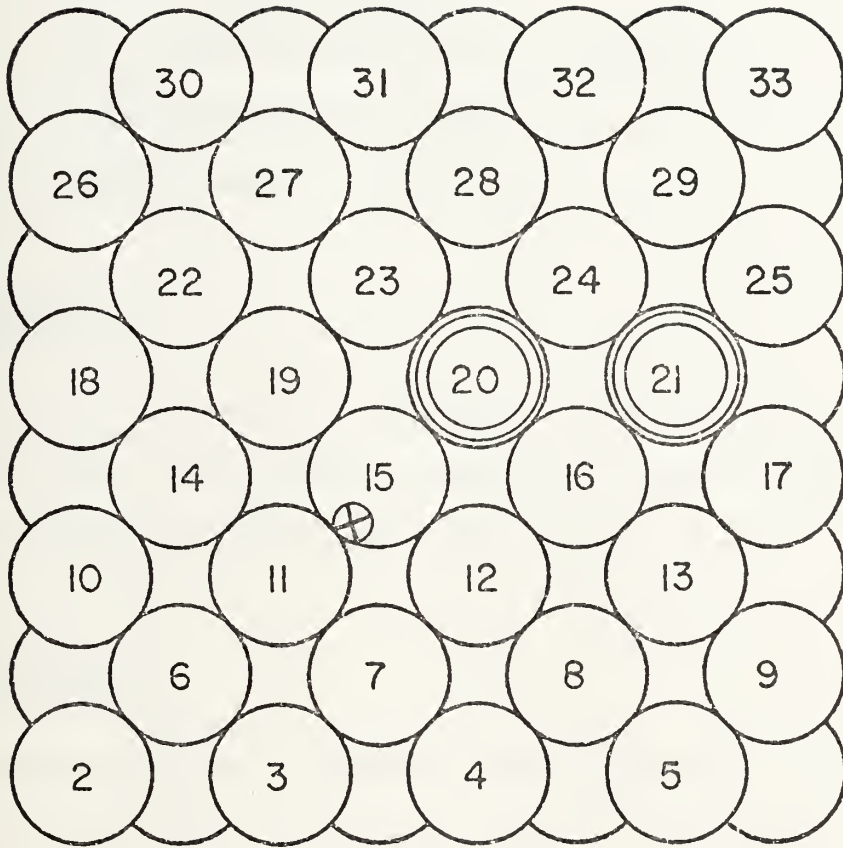
D #5

Initial Location of Dimer Atoms and Impact Point

Fig. 10

Initial Setup

8x4x8 copper crystal

129 atoms in fcc(100) orientation

Initial Energy of Argon Ion = 750 eV

Impact Point (2.7,0.0,2.5)

Timestep #30

The bullet ion has passed between atoms #11 and #15 driving them both downward and away from the point of impact. Atom #15 passes under atom #20 lifting it off of the surface.

Timestep #60

Atom #15 passes between second layer atoms #52 and #56. Atom #56 is pushed down and atom #52 is pushed up when #15 passes under it. With its upward motion, atom #52 pushes up on atom #21 popping it off of the surface in such a way that its position and velocity correspond with those of atom #20 and the two atoms form a dimer.

TRIMER MECHANISMS

Nomenclature	Atoms	
T #1	28-20-21	Fig. 11, page 41
T #2	18-22-27	Fig. 12, page 43
T #3	6-3-4	Fig. 13, page 45
T #4	39-7-40	Fig. 14, page 48

T #1

Initial Location of Trimer Atoms and Impact Point

Fig. 11

Initial Setup

      8x4x8 copper crystal

      129 atoms in fcc(100) orientation

      Initial Energy of Argon Ion = 750 eV
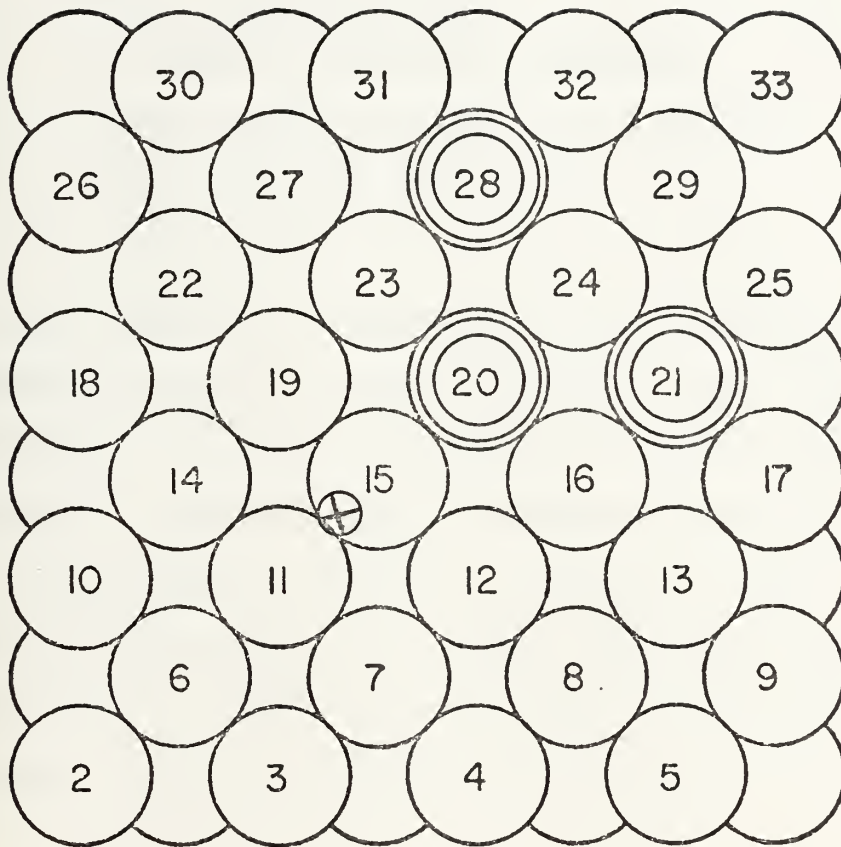
      Impact Point (2.7,0.0,2.6)

This mechanism is identical to the trimer formation mechanism as shown in detail in Chapter Two. While the preliminary simulation was run with only 32 atoms, the existence of the same type of cluster in the large crystal of 129 atoms leant credence to the small model copper crystal simulations. Notice that the effect of the larger crystal was to move the impact point slightly off of the diagonal [2.7,0.0,2.6) vs. (2.7,0.0,2.7)].

T #2

Initial Location of Trimer Atoms and Impact Point

Fig. 12

Initial Setup
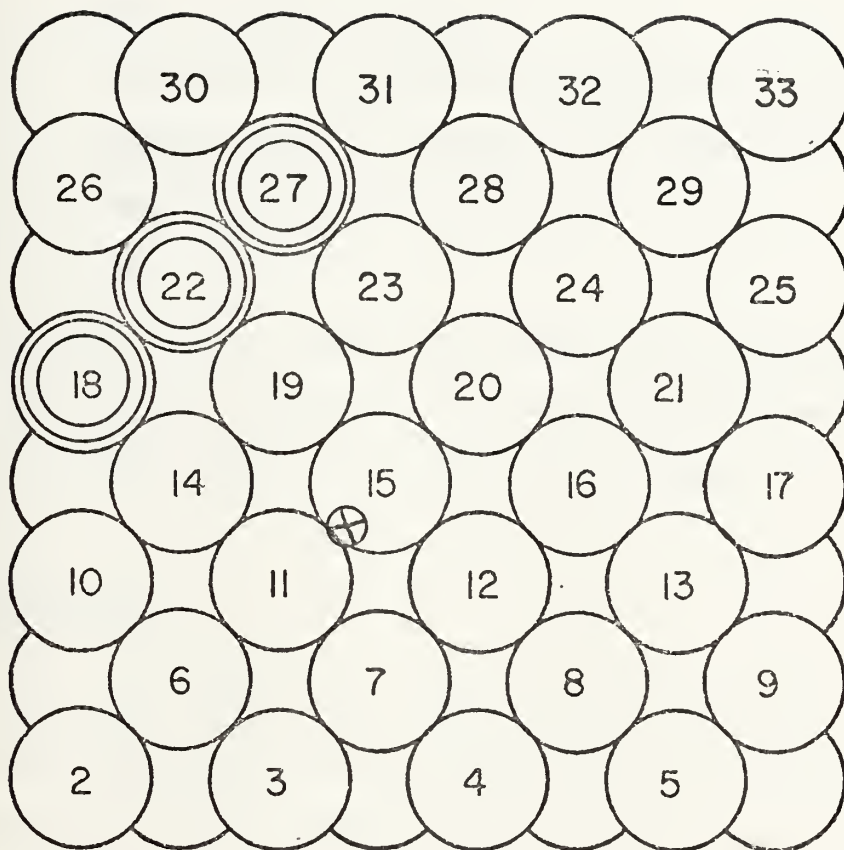
8x4x8 copper crystal

129 atoms in fcc(100) orientation

Initial Energy of Argon Ion = 1000 eV

Impact Point (2.7,0.0,2.6)

*Note that by simply increasing the ion energy from 750 eV (T #1) to 1000 eV, and keeping the same impact point, a new trimer formation mechanism was found.

Timestep #50

The bullet ion has passed between atoms #11 and #15 of the first layer and atoms #47 and #43 of the second layer. Atom #47 is moving downward and atom #15 has pushed atom #51 in the downward direction also.

Timestep #100

Atom #47 has now moved under atoms #50 and #55 giving them upward velocities toward the surface. Atom #18 is lifted off of the surface by atom #50 coming up from underneath while atoms #22 and #27 have been pushed away from the surface by the upward movement of atom #55. These atoms then move away from the surface as a trimer.

T #3

Initial Location of Trimer Atoms and Impact Point

Fig. 13

Initial Setup

8x4x8 copper crystal

129 atoms in fcc(100) orientation

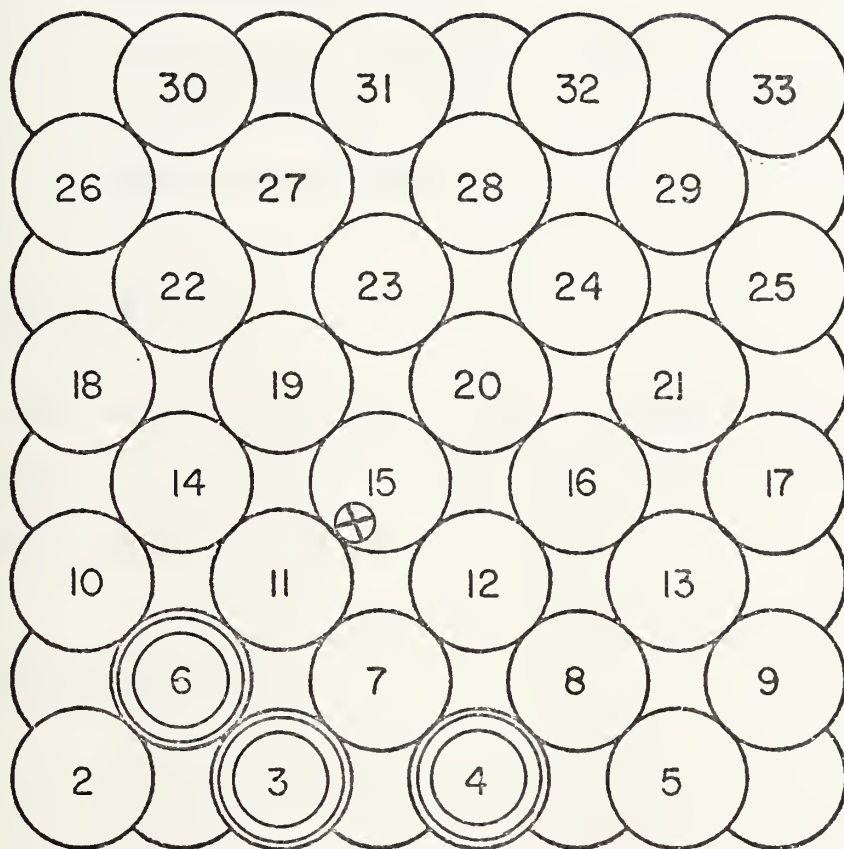Initial Energy of Argon Ion = 5000 eV

Impact Point (2.8,0.0,2.7)

Timestep #20

The bullet ion strikes atom #15 and drives it into the crystal. On recoil it passes under atom #11 lifting it up, and then pushes down on atom #43.

Timestep #40

The bullet ion has passed through the second layer lifting up atom #39. On recoil off of atom #39, while still moving downward, the bullet ion comes into contact with atoms #70 and #75 of the third layer.

Timestep #70

The bullet ion passes the third layer driving atom #75 down and atom #70 up. Atom #70 then pushes upward on atom #38.
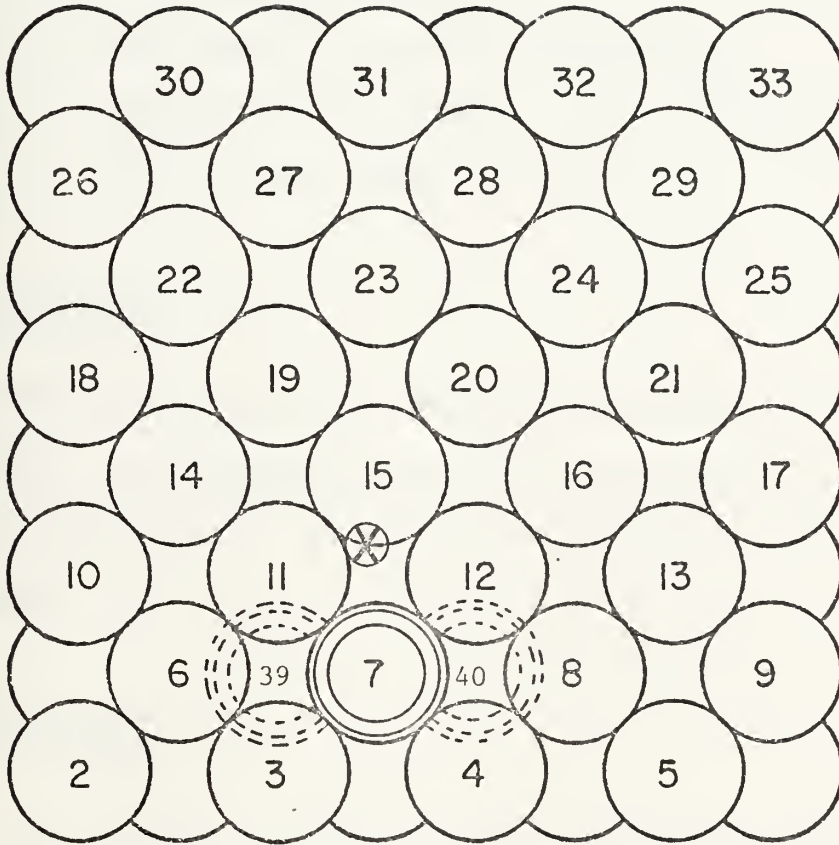
Timestep #130

Atom #11 is passing over atom #6 pushing it downward.
Atom #40 is coming up after atom #43, passes underneath;
and pushing atom #4 off of the surface. Atom #39 is pushing
up on atom #3.

Timestep #140

Atom #6 while moving in the downward direction comes
into contact with atom #38 moving up toward the surface.
Atom #6 recoils so strongly that it reverses direction and
comes up off of the surface and joins with atoms #3 and #4
to make a trimer.

Comment: Multimer formation is not limited to particular
atoms of the crystal. It is possible to move the impact
points from one atom to another and still produce an equiv-
alent multimer. The multimer will be made up of different
"number" atoms but the geometrical relationship will remain
the same. Sometimes minor adjustments in the initial energy
or the impact point were necessary to recreate multimers
that originally included "edge" atoms. For example, T #3
would also be produced for an impact point near (2.8,0.0,4.7)
with kinetic energy around 5000 eV but it would consist of
atoms (#14-#11-#12).

T #4

Initial Location of Trimer Atoms and Impact Point

Fig. 14

Initial Setup

8x4x8 copper crystal

129 atoms in fcc(100) orientation

Initial Energy of Argon Ion = 5000 eV

Impact Point (2.9,0.0,2.3)

Timestep #30

The bullet ion has passed through the first and second layers. On passing through the second layer it passed over atom #43 pushing it downward and under atom #47 lifting it upward.

Timestep #80

The bullet ion upon reaching the third layer pushes both atoms #71 and #79 downward. Atom #79 while moving downward passes under atom #76 and gives it an upward velocity.

Timestep #120

Atom #76 has pushed atom #40 upward toward the surface. Atom #40 in turn is pushing up on both atoms #7 and #4.

Atom #39 is lifted up toward the surface by the action
of one or more third layer atoms.

Atoms #40 and #7 are both moving away from the surface
and join with atom #39 to form a trimer.

IV. RESULTS

The computer simulation identified five mechanisms
of dimer formation and four mechanisms of trimer formation.
The simulation only investigated normal incidence of the
bullet ion with a small representative sample of impact
points. A more extensive effort which included oblique
incidence and a larger sample of impact points would undoubt-
edly uncover other formation mechanisms. The simulation
further revealed numerous mechanisms that produced groups of
two and three atoms that were "unbound" by only a small
fraction of an eV in positive potential energy. Simply by
varying incident energies and/or impact points, these possible
combinations could probably have been formed to bind together.

In an effort to establish patterns for multimer production
it is necessary to compare the mechanisms and note similari-
ties as well as differences between them. The simplest
mechanism appears to be a type that is similar to D #2, where
the bullet ion and the primary knock-on atom each lift up an
atom from the surface layer so that the two sputtered atoms
move away bound together.

The next type of mechanism would be one in which the
bullet pops up a surface atom, continues down to the second
layer of atoms where it lifts up an atom which on its upward
movement pops up another surface atom in such a manner that
it binds together with the originally sputtered atom. This

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type of mechanism can be extended downward to at least the fourth layer where a fourth layer atom pushes up on a third layer atom, which in turn pushes up on a second layer atom which in turn pops up a surface atom that joins with the one originally sputtered by the bullet (see D #3).

D #5 was a mechanism that showed atoms lifted off of the surface by the recoil of two different second layer atoms. It is not necessary for one of the atoms in a bound cluster to have been lifted off by the bullet ion. The simulation clearly showed that multimers could be formed by complex interactions of the bullet ion with various combinations of atoms from the first four layers of the crystal.

It is possible for atoms of any one of the four layers to be lifted upward by the motion of a penetrating bullet ion or target ion. The downward trajectory of a low energy particle can be depicted as shown in Fig. 15. From examination of this figure it is readily apparent that an atom often penetrates a layer by passing over one of the atoms, pushing that atom downward, and under the adjacent atom lifting that atom upward. If, however, the atom hits very close to the center of the atom pair these atoms could both be pushed in the downward direction (see Fig. 15b). This phenomenon influences the motion of an atom that travels through the crystal almost parallel to the surface layer. The atom is actually bumping along between the top and bottom layer, and driving every other surface layer atom upward.

(A)

(B)
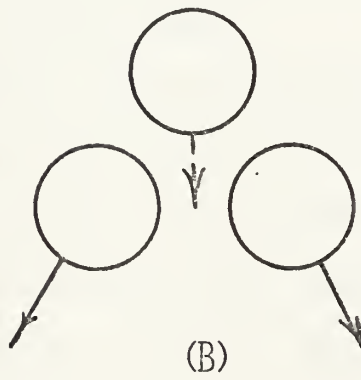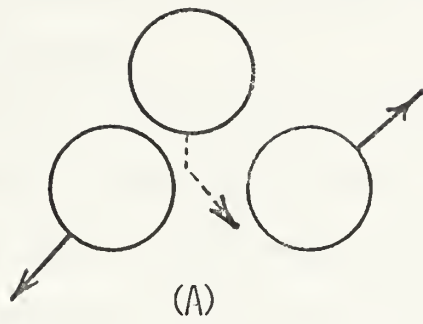
Layer Penetration Dynamics

Fig. 15

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With this analysis, it appears extremely unlikely that an atom will go along popping up clusters, as proposed in some theoretical speculations.

A simple computer simulation of a bullet ion striking a diatomic molecule in free space was run. If the bullet was not allowed to recoil (following earlier channel arguments), it was relatively easy to hit the molecule with a glancing collision in such a manner that the molecule would move off in a bound state. However, when atom recoil was allowed, it was not possible to hit the molecule so that it would move off as a bound dimer.

In the simulations using the microcrystallite, the bullet ion never produced a dimer by colliding successively with a pair of neighboring atoms. The sputtering of two nearest neighbor atoms by a chaneled atom therefore appears highly unlikely. Close analysis of the computer output in conjunction with Fig. 15 shows that it is more probable that channeled atoms produce dimers of two next-nearest neighbors.

Multimer production need not be limited to atoms of the surface layer or to any particular layer in general. For example, T #5 formed a trimer consisting of one surface layer atom bound with second layer atoms. The simulations yield data which suggests that multimers can consist of atoms from the surface layer on down to at least fourth layer atoms. Some "unbound" trimers and dimers consisting of third and fourth layer atoms were observed in the computer output but the probability of such multimer formation was extremely low.

The sensitivity to different initial kinetic energies of the bullet ion was also apparent. Highly energetic ions penetrate more deeply into the crystal and increase the probability that multimers will be formed via mechanisms including the lower layer atoms. A low energy ion only penetrates one or two layers, whereas a high energy (>1000 eV) ion transfers sufficient energy to the third and fourth layer atoms to cause these deep atoms to move upward pushing atoms, directly or indirectly, up off of the surface.

The choice of the potential used is a critical part of this type of simulation. A computer run was made using the NN(4) Anderman potential to compare the results with the NN(2) potential which was used for the majority of the simulation work. The Anderman NN(4) potential (see Ref. 5) reaches out to a greater distance (2.8 LU) thereby including atoms beyond the nearest neighhbor in the potential calculations. For an initial energy of 500 eV and an impact point of (2.625,0.0,2.3), the dimer was stable as in the previous run (see D #2). The mechanism found with the NN(4) potential was identical to the mechanism observed with the NN(2) potential, but the potential energy excess of the dimer decreased from -0.236 eV to -0.132 eV. Varying the potential function causes changes in the potential energy relationships but the mechanisms remain the same.

V. CONCLUSIONS

The results show that the sputtering of multimers from
a microcrystallite could be simulated for a bullet ion energy
range of 400 eV to 5000 eV. Examination of the data revealed
that particular mechanisms were applicable for a range of
energies and impact points. The use of different potential
functions to represent the interactions between the atoms
caused differences in the energetics of the mechanisms,
however the basic dynamics of the sputtering event did not
change.

While previous theories [7,8,0] suggested that nearest
neighbor atoms were the most likely to sputter as a dimer,
the simulation results do not substantiate this hypothesis.
The mechanism which sputtered atoms #15 and #29 (D #1) showed
that it was possible for atoms, initially separated by two
other atoms, to sputter and form a dimer, while mechanisms
D #2 to D #5 produced dimers from next-nearest neighbors.
Nearest neighbors can be sputtered as dimers but there appears
to be no preference for their production over other reasonable
combinations. So far, in fact, production of next-nearest
neighbor dimers seems to be predominant.

Early kinetic models went on the assumption that a
channeled atom would knock off two atoms in such a manner
that the sputtered atoms would remain bound. However the
detailed mechanisms did not show a single case in which the

two sputtered atoms (dimer) had been pushed up by the motions of a single atom.

The most surprising feature of the simulation was that it was possible for a bullet ion to lift off a surface layer atom directly in passing under the first layer and then lift up a second or third layer atom whose subsequent upward motion would also lift off a surface atom that would bind with the first atom sputtered earlier. This process allowed for the production of a dimer between atoms that were sputtered at quite different times. While there is probably a limit to the time interval allowed, it is clear that the sputs do not have to occur "almost simultaneously."

The computer simulation successfully isolated production mechanisms for dimers and trimers. While simulations of higher order multimers were not obtained, analysis of the sputs indicated that mechanisms for quadrimers and quintimers could probably also be achieved. These are necessarily low probability events; so their absence from the relatively small sample of possible events simulated here is not surprising.

From the details of the mechanisms described it is apparent that the dynamics of multimer production are extremely complex and do not lend themselves to simple explanations. Accordingly, a review of current analytic theories of multimer production seems appropriate.

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